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## Evolving patterns in boron cluster chemistry\*

Mark A. Fox and Ken Wade<sup>‡</sup>

Chemistry Department, University Science Laboratories, Durham, DH1 3LE, UK

**Abstract:** This paper outlines the development of our knowledge and understanding of the structures and bonding of boron cluster compounds, with particular reference to the evolving complementary roles localized bonding and molecular orbital treatments have played in providing simple rationalizations of their polyhedral molecules.

### INTRODUCTION: EARLY DEVELOPMENTS

The polyhedral patterns that characterize boron cluster chemistry have provided rich pickings for the structural and bonding enthusiast since they first become apparent, too rich to do justice to in a short paper. Here, we outline how those patterns and our attempts to understand them have evolved.

Life itself, at least as we know it, evolved in an electron-rich world, one in which there was such an abundance of electrons that our early ideas about valency assumed that at least two electrons, shared between a pair of atoms, were needed to form a covalent chemical bond between them [1]. Early boranes provided a challenge to this by existing despite their apparent electron deficiency. Compounds  $B_nH_{n+4}$  ( $n = 2, 5, 6$ , or  $10$ ) and  $B_nH_{n+6}$  ( $n = 4$  or  $5$ ), prepared in A. Stock's pioneering researches [2], in which he invented vacuum line technology to deal with these highly reactive substances, were labeled "electron-deficient" because they contained too few electrons to provide a pair for every 2-center link in their molecules, evident even before their molecular structures were determined. Containing  $(2n + 4)$  or  $(2n + 6)$  atoms respectively these borane molecules have only  $(2n + 2)$  or  $(2n + 3)$  valence shell electron pairs, fewer than the minimum number,  $(2n + 3)$  or  $(2n + 5)$ , of 2-center links required.

A real structural breakthrough was provided by R. P. Bell and H. C. Longuet-Higgins. They deduced the structure of diborane,  $B_2H_6$ , from its vibrational spectrum [3]. The value of the 3c2e bond concept, to explain its BHB links, soon followed.

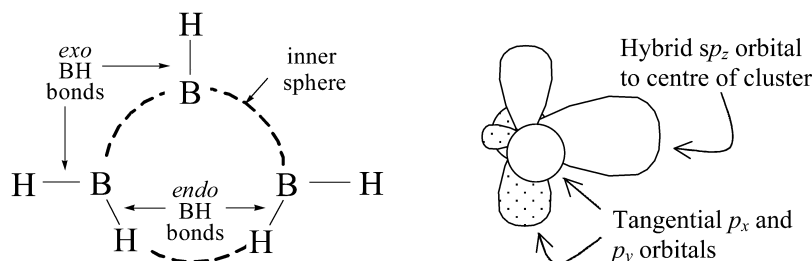
Subsequently, W. N. Lipscomb put borane structural chemistry on a sound basis by his classic low-temperature X-ray crystallographic studies of key boranes  $B_nH_{n+m}$  and perceptive analysis of the bonding implications of their intricate structures [4]. He noted that the  $n$  boron atoms and  $m$  (*endo*) hydrogen atoms lay on an inner, near-spherical surface; the remaining  $n$  (*exo*) hydrogen atoms lay on an outer sphere, attached to the boron atoms by 2c2e BH bonds pointing radially outwards from the cluster center. Bonding between the boron and *endo*-hydrogen atoms on the inner sphere involved  $(2n + m)$  electrons (two from each BH unit, one from each *endo*-hydrogen) which Lipscomb allocated to four types of localized electron pair bonds,  $s$  BHB and  $t$  BBB 3c2e bonds and  $y$  BB and  $x$  BH 2c2e bonds. Electron, orbital, and boron atom counts led to three equations linking the values of  $s$ ,  $t$ ,  $y$ , and  $x$  to  $n$  and  $m$ :

$$s = m - x = n - t = 2y + x$$

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<sup>‡</sup>Corresponding author

Solving these (three equations, four unknowns) gave ranges of *styx* values for particular values of  $n$  and  $m$ , including bond networks corresponding to known structures, alternatives through which these might rearrange, and likely networks for compounds of unknown structure.



Though it was not then apparent—too few pieces of the structural jigsaw puzzle were available when Lipscomb developed his *styx* rules for borane bonding—the total number of electron pairs holding the boron and hydrogen atoms together,  $s + t + y + x$ , (now referred to as the number of **skeletal electron pairs, SEPs**) when compared to the number of boron atoms, was to provide the key to the 3-dimensional shapes of borane clusters [5]. At the time, in the 1950s, the boron frameworks in boranes were regarded as icosahedral fragments, because elemental boron crystallized as  $B_{12}$  icosahedra in its allotropes. The square pyramidal structure of  $B_5H_9$ , clearly not an icosahedral fragment, was rationalized as a fragment of another boron polyhedron, the  $B_6$  octahedron, known in some metal borides.































## DELTAHEDRAL STRUCTURAL PATTERN

The full range of deltahedra on which borane structures are based became apparent with the discovery (in the 1950s space-race search for high-energy organoborane rocket fuels) of carboranes. R. E. Williams [6] (small carboranes) and M. F. Hawthorne [7] (large carboranes) were leading figures in carborane research from the start. Though the first large carboranes prepared had icosahedral structures, the existence of small carboranes  $C_2B_{n-2}H_n$  ( $n = 5, 6$ , or  $7$ ) with bipyramidal exclusively triangular-faced structures showed that other deltahedra than the icosahedron or octahedron had to be accommodated in any theory of borane cluster shapes. The structural pattern took time to unravel. X-ray diffraction methods could not always be used, were then very slow, and occasionally unreliable for these “light atom” molecules. NMR methods were in their infancy, and mistakes were made. However, by 1971 the generality of the deltahedral pattern of borane and carborane structures was substantiated by many examples, and Williams was able to publish that pattern [8] and gain general public recognition of its validity.

The main features of the structural pattern (shown in extended form here) are now standard textbook items. Borane dianions  $[B_nH_n]^{2-}$  and isoelectronic carboranes  $C_2B_{n-2}H_n$ , etc., known as *closo*-species, have the exclusively deltahedral skeletal structures shown in the left-hand column. Their  $n$  skeletal boron and/or carbon atoms lie on a spherical or nearly spherical surface, with skeletal connectivities  $k$  (numbers of nearest neighbor skeletal atoms) which range from 3 to 6. The carbon atoms of carboranes preferentially occupy the sites of lower  $k$  where more than one type of site is available, as when  $n = 5, 7-11, 13$ , or  $14$ .

*Nido*-species  $B_nH_{n+4}$ ,  $C_2B_{n-2}H_{n+2}$ , etc. have skeletal structures seen as fragments of the *closo*-deltahedra with  $(n + 1)$  vertices in which one high  $k$  site is left vacant (middle column). Their carbon atoms preferentially occupy sites of lower  $k$ , and their *endo*-hydrogen atoms occupy sites, normally BHB bridging sites, around the open face of the polyhedral fragment.

*Arachno*-species  $B_nH_{n+6}$ ,  $C_2B_{n-2}H_{n+4}$  etc. have skeletal structures based on the deltahedra with  $(n + 2)$  vertices on which two adjacent vertices have been left vacant (right-hand column). Their *endo*-hydrogen atoms occupy BHB or *endo*-BH sites around the open face.

<i>clos</i>	<i>nido</i>	<i>arach</i>	SEP
 5	 4	 3	<b>6</b>
 6	 5	 4	<b>7</b>
 7	 6	 5	<b>8</b>
 8	 7	 6	<b>9</b>
 9	 8	 7	<b>10</b>
 10	 9	 8	<b>11</b>
 11	 10	 9	<b>12</b>
 12	 11	 10	<b>13</b>
 13	 12	 11	<b>14</b>
 14	 13	 12	<b>15</b>

**Fig. 1** The deltahedral pattern, showing atom and SEP numbers.

Since Williams first described the pattern in 1971 [8], many new examples of all three categories of cluster and some others, such as *hyperclos*-species  $B_nX_n$  with  $n$  atoms and  $n$  SEPs or *hypho*-species  $B_nH_{n+8}$ , with  $n$  atoms and  $(n + 4)$  SEPs, have been prepared and structurally characterized, and some systems that appeared anomalous have been shown to conform to the pattern and not to have the originally assigned structures. Many new structures have been determined by X-ray or electron diffraction [9–11]. A very important development has been the use of IGLO/GIAO (individual gauge for localized orbital and gauge-independent atomic orbital) methods of structure determination [12,13], whereby experimental NMR chemical shift data have been compared with predicted chemical shifts

calculated for various possible structures. Indeed, ab initio calculations of borane/carborane structures are now so reliable as to allow the relative stabilities of different structural isomers of a given compound to be calculated with great precision, so allowing the site preferences of skeletal carbon atoms (**k**, adjacent/nonadjacent) and *endo*-hydrogen atoms (BHB or BH) to be placed on a quantitative basis [14].

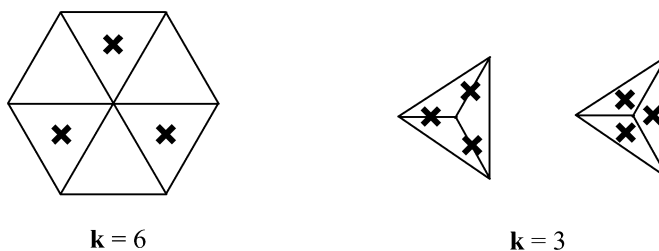
Most of Williams' early generalizations [8] have been vindicated subsequently, though the correspondence of the skeletal structures of some *nido*- and more *arachno*-species to the precise shapes and atom connectivities shown has proved less clear-cut than it seemed when the deltahedral fragment model was first proposed. It is, therefore, best to classify compounds as *closo*-, *nido*- or *arachno*-according to their formulae, noting departures from expected structures where these occur.

## BONDING TREATMENTS

**Molecular orbital (MO) treatments** of the bonding in *closo*-clusters are more helpful than localized bond treatments in indicating why  $(n + 1)$  SEPs are needed for  $n$ -atom deltahedral systems like  $[B_nH_n]^{2-}$  or  $C_2B_{n-2}H_n$ . Each skeletal atom provides three atomic orbitals (AOs) for skeletal bonding, best thought of as an  $sp_z$  hybrid AO, radially oriented toward the cluster center, and a pair of  $p$  AOs ( $p_x$ ,  $p_y$ ) oriented tangential to the pseudospherical cluster surface [4,5,15]. These latter  $2n$  AOs interact to generate  $n$  skeletal bonding MOs, to some of which out-of-phase combinations of radial AOs contribute. The radial AOs in turn contribute only one further bonding MO, of A symmetry, resulting from their fully in-phase combination, so explaining the need for  $(n + 1)$  SEPs. The exclusively triangular faces of the *closo*-structures maximize the number of bonding contacts between the skeletal atoms, a requirement demonstrated by A. J. Stone in a tensor surface harmonic treatment [16] that, in our opinion, provides the greatest insight into the skeletal bonding in borane-type clusters. The  $\sigma$ - and  $\pi$ -type interactions between the tangentially oriented  $p$  AOs illustrate the effectively 3-dimensional aromaticity of these systems [4,5], a point taken up by several workers, notably P. v. R. Schleyer [16–21]. Other notable contributions were made earlier by Longuet-Higgins and Roberts, who predicted, from MO arguments, that icosahedral  $[B_{12}H_{12}]^{2-}$  would be stable as the dianion before it was first prepared [22], and by Hoffmann and Lipscomb who carried out seminal MO studies on various species  $[B_nH_n]^{2-}$  [23].

A further valuable feature of MO treatments of the bonding in *closo*-species  $[B_nH_n]^{2-}$  is that they allow the identities of the **frontier orbitals** (HOMO and LUMO) to be established. Normally complementary (where one is bonding, the other is antibonding, and vice versa) these orbitals show what similar distortions will occur on adding or removing one or more electrons. Generally also degenerate, they allow one to understand that significant distortion is needed if adding or removing two electrons is not to leave a diradical. Where they are nondegenerate (as when  $n = 8$  or  $9$ ) systems containing  $n$  atoms held together by  $n$  or  $(n + 2)$  SEPs instead of  $(n + 1)$  SEPs are possible that retain the deltahedral shape of the *closo*-species, albeit expanded to a less spherical shape. The neutral ("hyper*closo*") halides  $B_8Cl_8$  and  $B_9Cl_9$  [24] are examples. Adding two electrons to a *closo*-system normally, of course, causes distortion not to an expanded *closo*-shape but to the deltahedral fragment *nido*-shape recognizably related to the next deltahedron in the *closo*-series.

MO treatments allow one to understand the apparently anomalous regular tetrahedral cluster shape found in  $B_4Cl_4$ ,  $P_4$  and many metal carbonyl clusters held together by four or six SEPs rather than the five SEPs that an  $(n + 1)$  rule might have seemed to imply for this the smallest deltahedron. The three AOs provided by each skeletal atom in such systems generate bonding MOs of A, T, and E symmetries, the A and T sets being occupied in the case of  $B_4Cl_4$  and  $Fe_4(CO)_{12}$ , the A, T, and E sets being filled in the case of a molecule like  $P_4$  or  $Co_4(CO)_{12}$ . Tetrahedral clusters held together by six SEPs can of course be regarded, somewhat artificially, as *nido*-species based on a trigonal bipyramidal parent deltahedron in which, unusually, a low connectivity (axial) vertex has been left vacant. **Localized bond treatments** for tetrahedral clusters work well. If there are four SEPs, these can be allocated to four 3c2e bonds in the four faces of such clusters, whereas six SEPs can be allocated to six bonds along



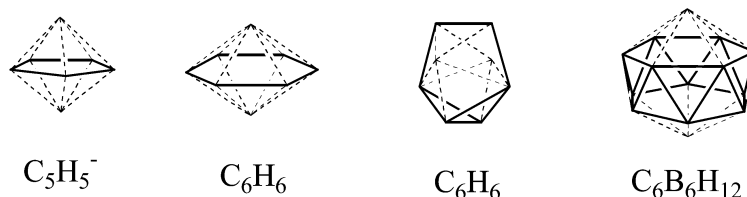
the six tetrahedron edges. Significantly, tetrahedral metal carbonyl hydrides  $M_4H_4(CO)_{12}$  have face-bridging hydrogen atoms when there are four SEPs ( $M = Mn$ ), edge-bridging hydrogen atoms when there are six SEPs ( $M = Fe$ ).

For higher deltahedra, **LB** treatments are of less value. The *styx* rules reduce to  $t = (n - 2)$  3c2e BBB bonds and  $y = 3$  2c2e BB bonds for anions  $[B_nH_n]^{2-}$ . Fitting these to selections of the  $(2n - 4)$  faces and  $(3n - 6)$  edges of the *closo*-deltahedra leads to extensive scope for resonance (aromaticity [24]) but gives little feeling for the distribution of the SEPs except in one respect, which is the relationship between skeletal connectivity **k** and the bond networks by which atoms can bond to their **k** neighbors [25]. An atom with **k** = 6 would have to use its three AOs exclusively in 3c2e bonds to link to all six neighbors (above left), whereas an atom with **k** = 3 could be involved in three 2c2e bonds or three 3c2e bonds (above right). The types of bonds used have charge implications. A BH unit supplying two electrons for skeletal bonding will remain neutral if involved in three 3c2e BBB bonds, but acquire a negative charge of  $-0.5e$  if resonating between three 3c2e BBB bonds and three 2c2e BB bonds. One can, therefore readily understand why the sites of lower connectivity (which can use more 2c2e bonds) are more negatively charged in *closo*-dianions  $[B_nH_n]^{2-}$ , or why the carbon atoms, being more electronegative than boron atoms, tend to occupy the sites of lower connectivity in carboranes such as  $C_2B_3H_5$ ,  $C_2B_5H_7$ ,  $C_2B_6H_8$ , etc.

Lipscomb's *styx* treatment, developed for *nido*- and *arachno*-boranes, remains of considerable value not only for boranes  $B_nH_{n+m}$  ( $m = 4$  or  $6$ ), but also for isoelectronic carboranes when 3c2e CBB, CCB, or even occasionally CHB bonds are added to the range of 3c2e bonding possibilities. The more electronegative carbon atoms occupy lower connectivity sites around the open face of the deltahedral fragment structures where they can participate in as few 3c2e bonds as possible. The tendency of *endo*-hydrogen atoms to be associated with BHB bonds around the open face is intelligible if one thinks of such bonds as resulting from protonation of 2c2e BB bonds in the hypothetical precursor anions  $[B_nH_n]^{4-}$  or  $[B_nH_n]^{6-}$  from which the neutral molecules  $B_nH_{n+4}$  or  $B_nH_{n+6}$  are formally derived [26,27]. The scarcity of CHB bonds and absence of CHC bonds is intelligible in that the availability of the 2c2e bond electron density for protonation decreases in the sequence  $BB > BC > CC$ . The preference of *endo*-hydrogen atoms to occupy BHB sites peripheral to open faces in *nido*- or *arachno*-species may force carbon atoms into nonperipheral sites [14,28].

An appreciation of how a parent deltahedral *closo*-species  $[B_{n+1}H_{n+1}]^{2-}$  can be converted into a neutral *nido*-fragment  $B_nH_{n+4}$  is, however, better achieved using MO arguments than by localized bond treatments, particularly if one treats the conversion in two stages [15]. The first stage involves removal of a  $[BH]^{2+}$  unit from the vertex to be vacated, so generating a *nido*-shaped (hypothetical) anion  $[B_nH_n]^{4-}$  with the same number of SEPs as in the parent *closo*-system. The second stage involves the addition of four protons in a suitable array to match the sites finally occupied by the *endo*-H atoms in the neutral molecule  $B_nH_{n+4}$ . In MO terms, removal of the  $[BH]^{2+}$  unit from the parent *closo*-deltahedral dianion  $[B_{n+1}H_{n+1}]^{2-}$  destabilizes those skeletal bonding MOs to which the AOs of the departing  $[BH]^{2+}$  unit contributed. Those destabilized MOs are then restabilized by the four protons, effectively functioning as an isolobal replacement for the lost  $[BH]^{2+}$ .

Extensions of such arguments allow removal of a second  $[BH]^{2+}$  unit from the hypothetical *nido*-anion  $[B_nH_n]^{4-}$  to form a hypothetical *arachno*-anion  $[B_{n-1}H_{n-1}]^{6-}$  which can then be converted into



the neutral *arachno*-species  $B_{n-1}H_{n+5}$  by bringing up six protons in suitable array to compensate for the two  $[BH]^{2+}$  units lost. Calculations [27] suggest that the second  $[BH]^{2+}$  unit removed should be from another high-connectivity vertex remote from the first but that the six protons needed to form the neutral borane can compensate for the loss of two  $BH^{2+}$  units more effectively if these are lost from adjacent (not necessarily both high connectivity) vertices. It is thus the six *endo*-hydrogen atoms that have to be accommodated in neutral *arachno*-boranes  $B_nH_{n+6}$  that are responsible for the “adjacent-vertex” feature of the borane structural pattern. Where these *endo*-hydrogen atoms are not present, nonadjacent vertices may be left vacant, as in the case of that ultimate 5-atom 8 SEP *arachno*-anion,  $[C_5H_5]^-$  (analogous to the hypothetical  $[B_5H_5]^{6-}$ ), in benzene or benzvalene (6 atoms, 9 SEPs) or in the 12-atom 15 SEP hexacarbaborane  $C_6B_6H_{12}$  [29] (formally analogous to the hypothetical anion  $[B_{12}H_{12}]^{6-}$ ). That it is **high-connectivity vertices** that are preferably left vacant on going from the parent *closo*-deltahedron to the *nido*-species, and later to the *arachno*-species, may appear surprising since such processes break more links between skeletal atoms than removing atoms from low *k* sites, whereas the *closo*-species have deltahedral structures in order to **maximize** the number of links. Rationalizations include the greater scope for *endo*-hydrogen atoms to stabilize the larger open face when adjacent vertices are left vacant, the greater stabilization afforded by the greater number of skeletal atoms around the open face, and the argument that the higher the connectivity of the  $[BH]^{2+}$  unit formally removed, the lower its share of the electron density, and so lower the energy needed to remove it.

The positions of the *endo*-hydrogen atoms around the open faces of *nido*- and *arachno*-species, predictable from the frontier orbital characteristics of anions  $[B_nH_n]^{4-}$  and  $[B_nH_n]^{6-}$ , [27] deserve further comment. In *nido*-species  $B_nH_{n+4}$ , the *endo*-hydrogen atoms are normally found in BHB bridging sites, whereas in *arachno*-species  $B_nH_{n+6}$ , some *endo*-hydrogen atoms are forced to occupy clearly less desirable terminal sites, where they effectively isolate, in a localized *endo*-BH bond, a pair of electrons otherwise available for bonding between skeletal boron atoms. This feature can generate misunderstanding of the term “skeletal electron pairs”, which is taken by some to refer only to those electrons involved in bonding between the skeletal atoms [30]. However, it applies to the bonding between **all** of the atoms, whether B, C, or H in boranes and carboranes, that lie on the inner spherical surface Lipscomb focused attention on, i.e., all of the valence shell electron pairs in boranes and carboranes except for those involved in the *exo*-BH or CH bonds.

Where an *endo*-BH unit is found in an *arachno*-borane, it therefore represents, in protonated form, a pair of electrons that would have been a lone pair on a specific atom in the hypothetical anion  $[B_nH_n]^{6-}$ , occupying an AO tangential to the spherical surface on which the skeletal atoms lie, so included in the SEP count though not playing a bonding role between the skeletal atoms. If localized bond treatments are to be retained for *arachno*-species  $[B_nH_n]^{6-}$  or more open clusters, particularly those with few or no *endo*-hydrogen atoms, it would be helpful to identify the localized electron pairs as associated with one, two, or three skeletal atoms. For example, Lipscomb’s *styx* approach, already adapted by Williams to become a *Stx* approach ( $S = s + y$ ) [31], could be further adapted to become a “*tyx*” system, in which *t* retains its original significance (the number of 3c2e bonds between skeletal atoms), *y* represents the sum of Lipscomb’s original *s* and *y* (i.e., the number of 2c2e bonds between pairs of skeletal atoms, whether protonated or not) and *x* represents the number of SEPs associated with individual atoms (lone pairs). Orbital and electron counts for anions  $[B_nH_n]^{c-}$  show that  $3n = 3t + 2y + x$  and  $(2n + c) = 2(t + y + x)$ .

The *closo*-, *nido*-, *arachno*-pattern illustrated earlier in this paper shows the deltahedral and deltahedral fragment skeletal structures expected for clusters with from 3 to 14 skeletal atoms formally held together by from 6 to 15 SEPs. The pattern holds well but not perfectly for systems containing from 7 to 13 SEPs (those in Williams' original paper [8]), but exceptional structures, different from those shown, are not uncommon among systems with 6 SEPs (such as the tetrahedral clusters already discussed) or with 14 or 15 SEPs, where energy differences between alternative structures are less. The main defect of Williams' original part of our figure is that it misrepresents the geometry of *nido*-B<sub>8</sub>H<sub>12</sub>-related systems, which have an *arachno*-B<sub>8</sub>H<sub>14</sub>-type geometry. Williams has explained this in terms of vertex homogeneity [32]. The geometry observed for B<sub>8</sub>H<sub>12</sub> has higher symmetry with fewer connections and more homogeneous vertices than the "expected" geometry. However, the *nido*-geometry found for B<sub>9</sub>H<sub>13</sub>-related species also poses a similar problem; the vertex homogeneity argument would favor the alternative geometry with 3-fold symmetry found for *arachno*-B<sub>9</sub>H<sub>15</sub>-related species. Williams applied the localized bond treatment (*styx*) to the latter geometry to show that no such framework can be drawn with a *nido*-count. Our own computations on the *arachno*-B<sub>9</sub>H<sub>9</sub><sup>6-</sup> geometry suggest that the degeneracies of the frontier orbitals explain why *nido*-9-vertex systems do not have this shape; a species [B<sub>9</sub>H<sub>9</sub>]<sup>4+</sup> with that geometry would not be a closed-shell species, but a diradical.

## CONCLUDING COMMENTS

Our knowledge and understanding of borane and heteroborane cluster chemistry has developed enormously over the three decades since Williams first described the deltahedral structural pattern in 1971. Most of the essential features he described then remain valid today, extended to series of compounds with from 6 to 15 skeletal electron pairs holding together from 3 to 14 skeletal atoms, and both MO and localized electron pair treatments of the bonding have value in understanding the roles these SEPs play. Methods of structural characterization, experimental and theoretical, have advanced enormously; model hypothetical systems can now be treated with confidence—at least for the light elements (e.g., boron, carbon, and hydrogen)—and the insight these systems provide for cluster chemistry in general has proved extremely valuable [5,10,11,15,17,33,34]. We plan to discuss the area more fully in a future article in which there will be space to cover areas neglected here, such as metallaboranes [34], alternative polyhedra [35], azaboranes [36], and other heteroboranes, fused polyhedral systems [37], and other categories of cluster related to boranes by isolobal analogies [38]. Borane cluster chemistry remains an exciting, developing, pattern-making area in which to test both simple and sophisticated bonding and geometric treatments.

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